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Rotational State Distribution of NO after Collisions with Fast Hydrogen Atom

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Based on the collisional time-correlation function approach a general analytical expression has been derived for the double differential cross-section with respect to the scattering angle and the final rotational energy, which can be applied to molecules with non-zero electronic orbital angular momentum after collision with fast hydrogen atoms. By integrating this expression another very simple expression, which gives the final rotational distribution as a function of the rotational quantum number, has also been derived. When this expression is applied to $NO(^2\Pi_{1/2}, v'=1)$ and $NO(^2\Pi_{3/2}, v'=1, 2, 3)$, it can reproduce the experimental rotational distribution after collision with fast H atom very well. The average rotational quantum number and average rotational energy calculated using this expression are also in good agreement with those deduced from the experimental distributions.

Introduction

Several years ago we derived an expression for the double differential cross section (with respect to scattering angles and final rotational energies) of molecules with a thermal distribution of initial rotational states colliding with fast atoms.[1] This expression, based on the collisional time-correlation function formalism, is valid when the collision time is short compared with the periods of internal motions of target molecules.

The formulation gave a simple final rotational distribution in terms of the error function, which can be used to parametrize experimental results. The derived expression was applied to the experimentally measured final rotational distributions of $^1\Sigma$ electronic state molecules CO and CO_2 colliding with fast hydrogen atoms,[2,3] for which the total electronic angular momentum is zero. It was found that for $CO(v'=1)$ and $CO_2(00^01)$, in which the collisions are impulsive, the derived formula fitted the experimental results very well. For $CO(v'=0)$, in which long-duration, complex-forming collisions play an important role, however, an additional statistical distribution as suggested by surprisal analysis[4] was necessary

to explain the experimental distribution satisfactorily.

There have been continued interests in the collisional energy transfer between fast, mono-energetic hydrogen atom (H or D) and simple diatomic or triatomic molecules such as CO,[5,6] NO,[7] H_2O[8] and CO_2.[9~13] In this work we have extended our theory and obtained a modified expression which can be applied to molecules with non-zero total electronic angular momentum and report the result for $H+NO(^2\Pi_{1/2}, {}^2\Pi_{3/2})$ collision systems.

Formulation

The rotational energy for Hund's case (a) molecules, neglecting centrifugal distortion terms, can be expressed as[14]

$$E_r = Bhc[J(J+1) - \Omega_t^2], \quad J \geq \Omega_t \tag{1}$$

where Ω_t is the component of the total electronic angular momentum along the internuclear axis and B is the rotational constant; h and c have their usual meanings.

With this expression replacing Eq. (14.e) in Reference 1 and all the E_r terms therein, the remaining derivation follows

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closely the procedure outlined in section II. B of Reference 1. Since the derivation is straightforward, we refer to Reference 1 for nomenclature and detailed procedure and we only point out the necessary modifications as follows.

$$I = b^{-1} \int_{b\Omega_e}^{\infty} \exp\left[-\left(\frac{z-x}{\sqrt{2a_2}}\right)^2\right] \exp(-x)dx$$

$$= \left(\frac{\sqrt{a_2}}{b}\right) \exp\left(\frac{a_2}{2}-z\right)\left(\frac{\pi}{2}\right)^{1/2} \mathrm{erfc}(t) \qquad (2)$$

$$E_r' = Bhc[J'(J'+1)-\Omega_e'^2] \qquad (3)$$

$$t = (b\Omega_e + a_2 - z)/\sqrt{2a_2} \qquad (4)$$

$$z = (E_r' - \langle\varepsilon_r\rangle)/(k_B T) \qquad (5)$$

$$b = Bhc/(k_B T) \qquad (6)$$

$$\frac{d^2\sigma}{dE_r d\Omega} = A \ \exp(a_1+\frac{a_2}{2}-x') \ \mathrm{erfc}[(a_1+a_2-x'+b\Omega_e)/\sqrt{2a_2}] \qquad (7)$$

$$x' = \frac{E_r'}{k_B T} = Bhc[J'(J'+1)-\Omega_e'^2]/(k_B T) \qquad (8)$$

$$a_1 = \langle\varepsilon_r\rangle/(k_B T) \qquad (9)$$

$$a_2 = \langle(\Delta\varepsilon_r)^2\rangle/(k_B T)^2 \qquad (10)$$
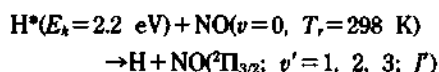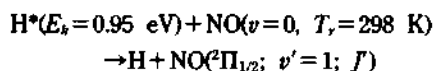
Here, the primed quantities refer to the final state.

The final expression for the scattering cross section for final rotational quantum number J' becomes

$$\sigma(J') = a_3(2J'+1)\exp(a_1+\frac{a_2}{2}-x')$$

$$\mathrm{erfc}[(a_1+a_2-x'+b\Omega_e)/\sqrt{2a_2}] \qquad (11)$$

Results and Discussion

In this section we present the final rotational distribution of a diatomic molecule with non-zero total electronic angular momentum after collision with fast hydrogen atom, obtained from the equations derived in the previous section. The specific collision system chosen for illustration is H+NO.

Wight et al.[7] determined the vibrational, rotational, and spin-orbit state distributions for inelastic collisions of NO molecules with H atoms employing laser-induced fluorescence technique. Their collision processes can be summarized as follows,

$$\mathrm{H^*}(E_k=0.95 \ \mathrm{eV})+\mathrm{NO}(v=0, \ T_r=298 \ \mathrm{K})$$
$$\rightarrow \mathrm{H}+\mathrm{NO}(^2\Pi_{1/2}; \ v'=1; \ J')$$

$$\mathrm{H^*}(E_k=2.2 \ \mathrm{eV})+\mathrm{NO}(v=0, \ T_r=298 \ \mathrm{K})$$
$$\rightarrow \mathrm{H}+\mathrm{NO}(^2\Pi_{3/2}; \ v'=1, \ 2, \ 3; \ J')$$

Here T_r is the rotational temperature of NO before collision.

Their experimental data together with the theoretical rotational distribution curves obtained by fitting Eq. (11) to the experimental points are shown in Figures 1 and 2. The numerical fitting procedure is the same as that outlined in Section II. C of Reference 1. The best fit parameters are collected in Table 1.

As is evident from Figures 1 and 2, the theoretical curves can reproduce the experimental results quite well except
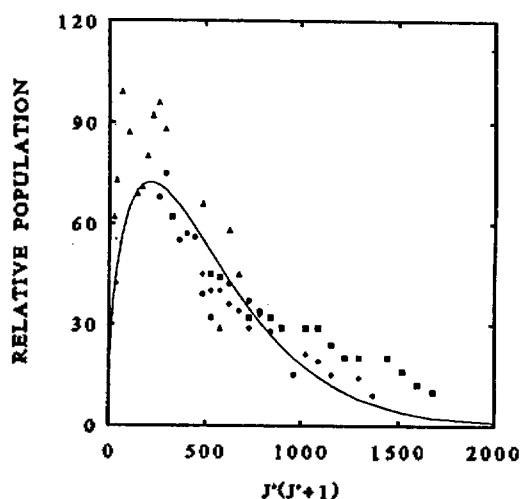
Figure 1. Final rotational state distribution for NO($^2\Pi_{1/2}$, $v'=1$) excited by 0.95 eV H+NO collisions. Experimental data are taken from Reference 7. The solid curve is the theoretical best fit from this work.
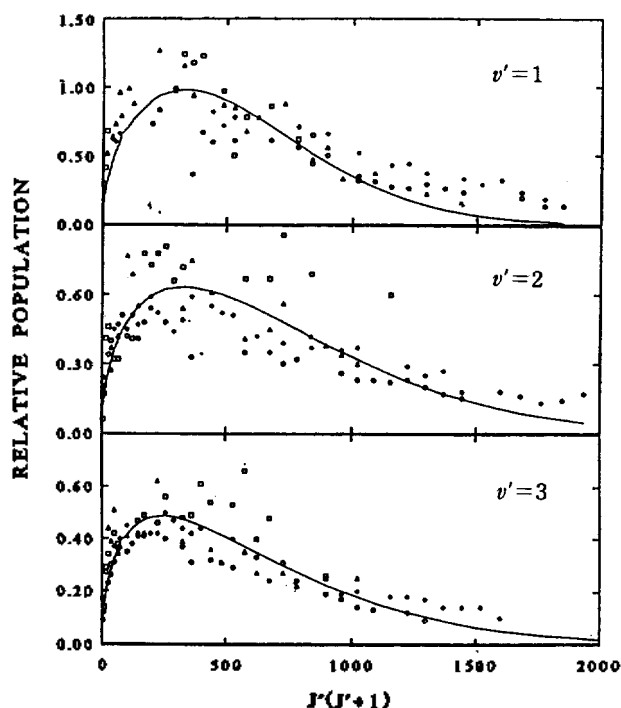
Figure 2. Final rotational state distribution for NO($^2\Pi_{3/2}$, $v'=1$, 2, 3) excited by 2.2 eV H+NO collisions. Experimental data are taken from Reference 7. The solid curve is the theoretical best fit from this work.

when J' is large; there the theoretical distribution is consistently lower than the experimental one. The same trend was observed earlier for the CO($v'=0$) rotational distribution after collisions with H($E_k=1.58$ eV)[1] and of CO($v'=1$ and 2) after collisions with H($E_k=2.3$ eV).[6] Also it seems that the theoretical fit is better for 2.2 eV than 0.95 eV collisions. Since our formalism is valid when the collisions are brief and impulsive, this fact is consistent with Colton and Schatz's

Table 1. Best Fit Parameters for Final Rotational Distribution of NO after Collision with Fast H atom

Vibronic state of NO	Best fit parameters		
	a_1	a_2	a_3
$^2\Pi_{1/2}(v'=1)$	-20.9	72.9	639
$^2\Pi_{3/2}(v'=1)$	-2.92	24.1	0.261
$^2\Pi_{3/2}(v'=2)$	-13.3	79.6	0.800
$^2\Pi_{3/2}(v'=3)$	-37.5	151	31.3

Table 2. Final Rotational State Characteristics for NO

State		Exp*	Theory	
			This work	Colton†
$^2\Pi_{1/2}$ $(v'=1)$	J'_{max}	not certain	13.5	
	$\langle J'\rangle$	18.5	18.5	24
	$\langle E_r'\rangle(cm^{-1})$	730	684	
$^2\Pi_{3/2}$ $(v'=1)$	J'_{max}	not certain	17.5	
	$\langle J'\rangle$	19.5	19.5	26
	$\langle E_r'\rangle(cm^{-1})$	862	763	
$^2\Pi_{3/2}$ $(v'=2)$	J'_{max}	not certain	17.5	
	$\langle J'\rangle$	19.5	19.5	29
	$\langle E_r'\rangle(cm^{-1})$	853	810	
$^2\Pi_{3/2}$ $(v'=3)$	J'_{max}	not certain	15.5	
	$\langle J'\rangle$	17.5	17.5	26
	$\langle E_r'\rangle(cm^{-1})$	699	662	

*deduced from the experimental data in Reference 7. † Reference 15. J'_{max}: The rotational quantum number at which the rotational state distribution shows its maximum.

$\langle J'\rangle$: Average rotational quantum number, $\sum_{J'} J'N_{J'}/\sum_{J'} N_{J'}$

$\langle E_r'\rangle$: Average rotational energy, $\sum_{J'} E_{J'}N_{J'}/\sum_{J'} N_{J'}$

finding that some of the cross section is due to HNO and NOH complex formation. In a detailed theoretical trajectory study they pointed out that complex formation is much more important at $E_k=0.95$ eV than at $E_k=2.2$ eV and also that complex forming collisions lead to hotter rotational distribution favoring large J' values than the direct collisions.[15]

In addition to the general shape of the theoretical curves, the goodness of the fit can be judged by various quantities characterizing the rotational distribution; some of them are: J'_{max}, which gives the rotational quantum number exhibiting maximum population, the average rotational quantum number $\langle J'\rangle$, and the average rotational energy $\langle E_r'\rangle$. These quantities are reported in Table 2.

From Table 2 one can see that $\langle J'\rangle$ values calculated from this work agree exactly with the fitted experimental data

while the classical trajectory results of Colton and Schatz give quite higher values for all four cases. Our calculated average rotational energies are within 5-12% of the experimental values, which we believe are within experimental error considering the wide scatter of the experimental points. Furthermore, the theoretical J'_{max}, which cannot be determined with certainty from the experimental data, may serve as a rough guide for analyzing the experimental data.

In conclusion we have derived an expression which gives the rotational state distribution of the molecules with nonzero electronic angular momentum after collision. We have also tested it for the H+NO collision system by fitting the theoretical parameters to the experimental data and it was found that the theoretical curves can reproduce the experimental data quite well.

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